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(54) **OXIDES OF NITROGEN GAS SENSORS AND METHODS**

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(21) Appl. No.: **11/162,251**

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(57) **ABSTRACT**

(52) **U.S. Cl.** **205/781**; 204/426; 204/429;
205/783.5; 205/784; 73/23.31; 73/23.32

Apparatus and methods for measuring NO_x concentrations are disclosed. One method includes the steps of providing a gas stream having a NO concentration and a NO₂ concentration, wherein a sum of the NO concentration and the NO₂ concentration is a total NO_x concentration; contacting the gas stream with a first zirconium oxide based oxygen sensor at a first temperature to achieve a first NO:NO₂ equilibrium at the first temperature; contacting the gas stream with a second zirconium oxide based oxygen sensor at a second temperature to achieve a second NO:NO₂ equilibrium at the second temperature; and determining the total NO_x concentration by measuring a response of the first zirconium oxide based oxygen sensor to achieve the first NO:NO₂ equilibrium and a response of the second zirconium oxide based oxygen sensor to achieve the second NO:NO₂ equilibrium. The second temperature is different than the first temperature.

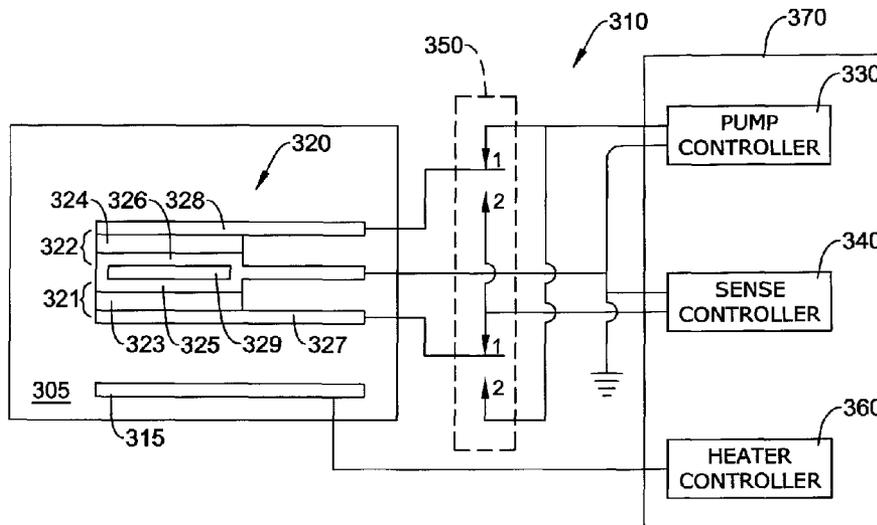
(58) **Field of Classification Search** 204/424-429;
205/783.5-785, 781; 73/23.31-23.32, 23.2
See application file for complete search history.

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7 Claims, 6 Drawing Sheets



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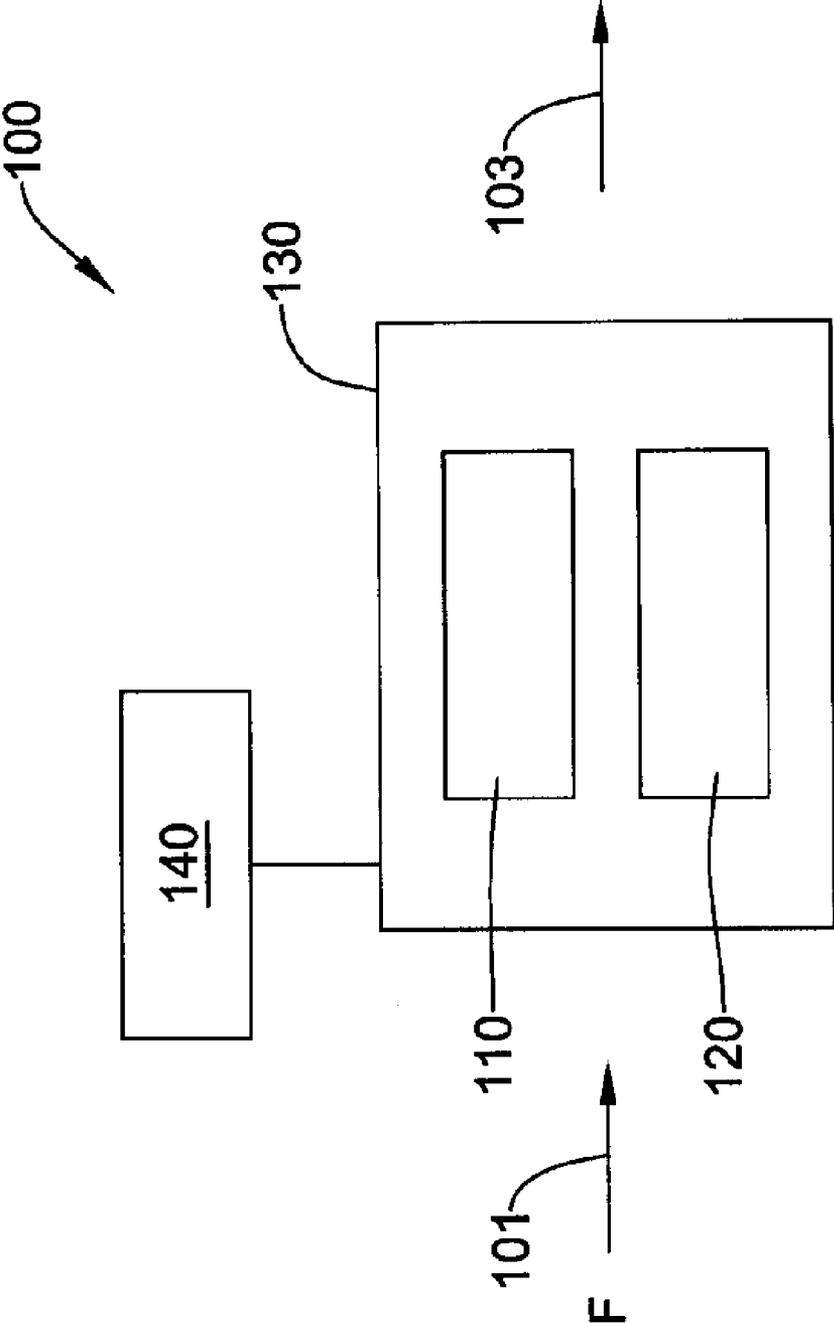


Figure 1

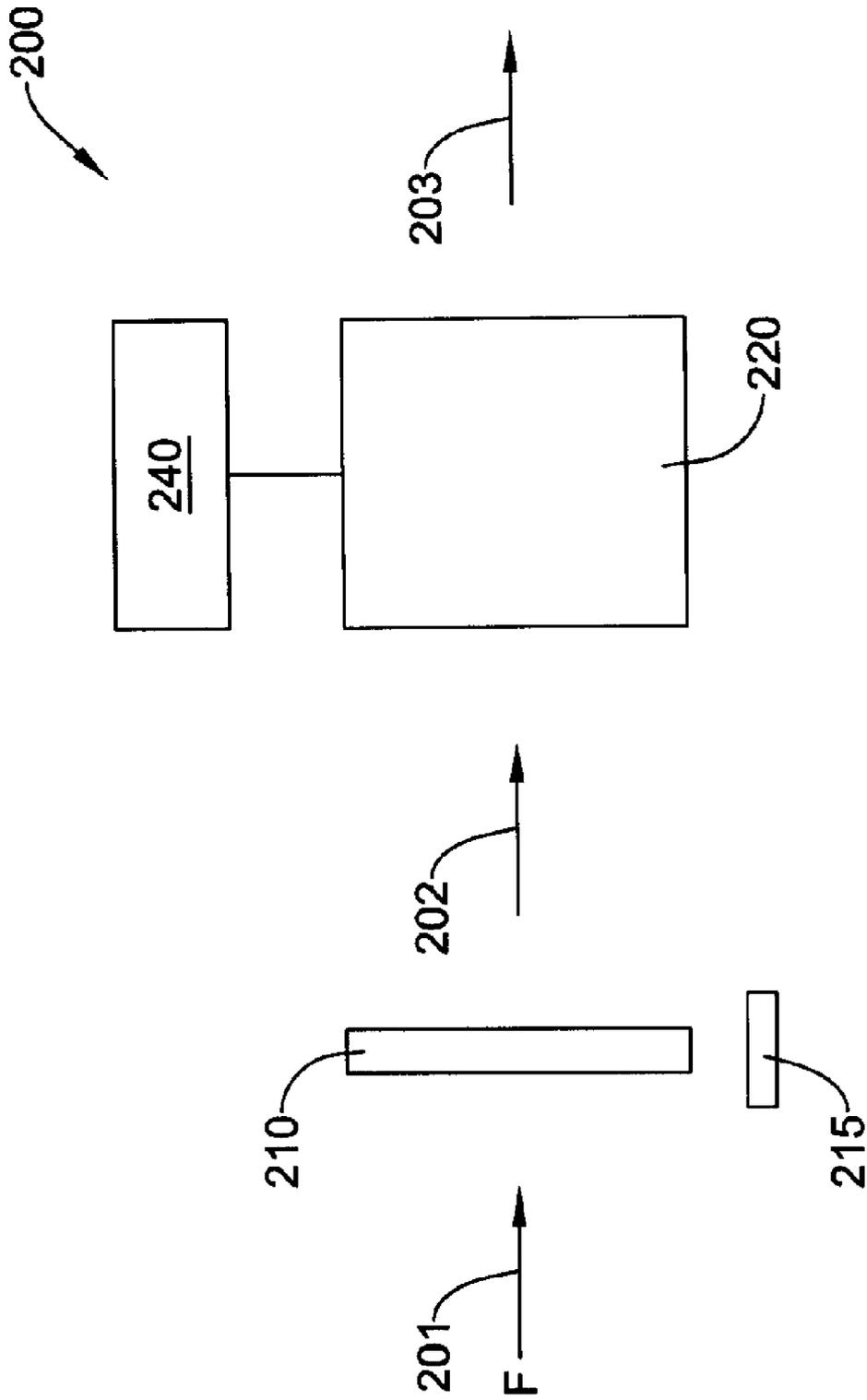


Figure 2

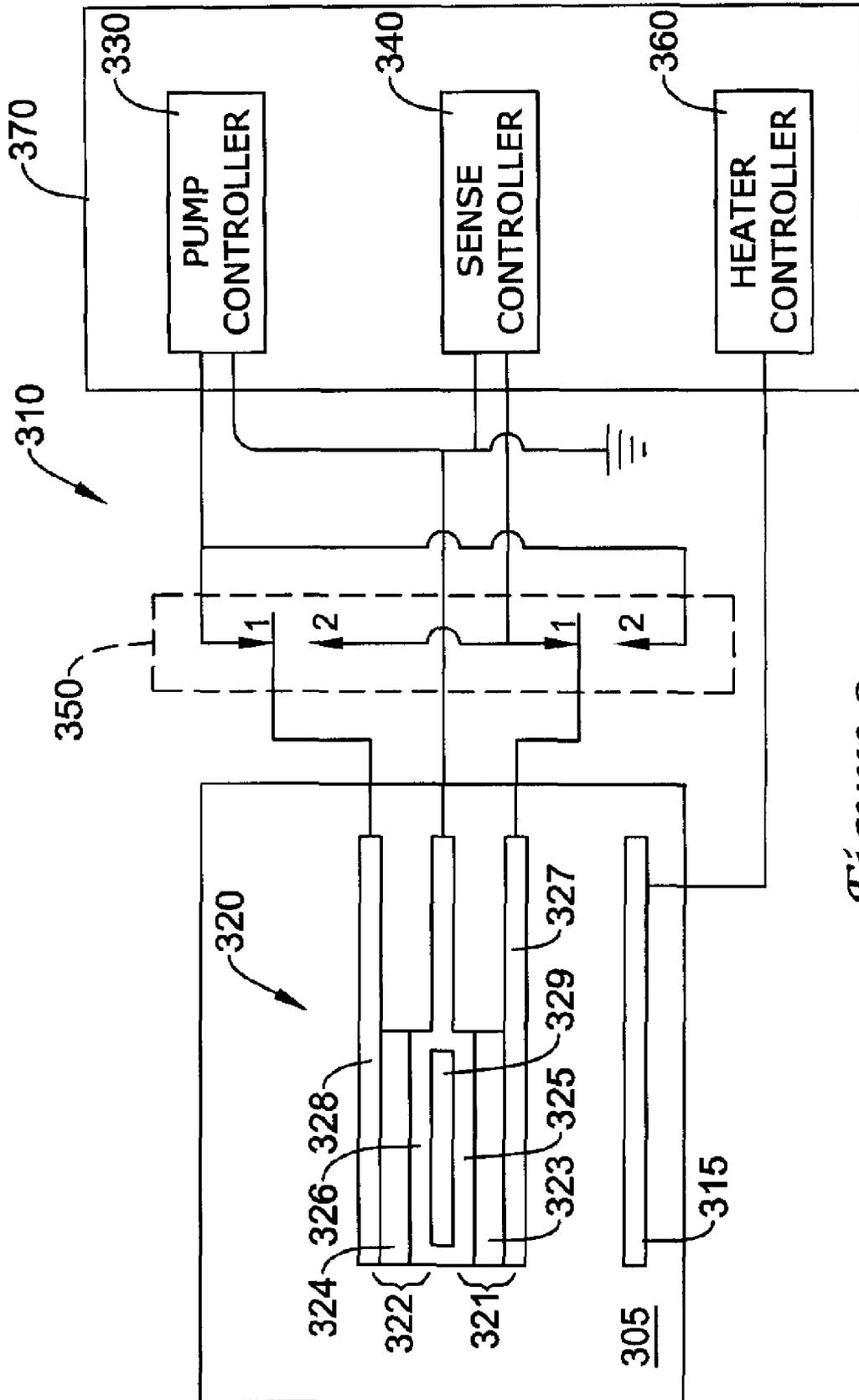


Figure 3

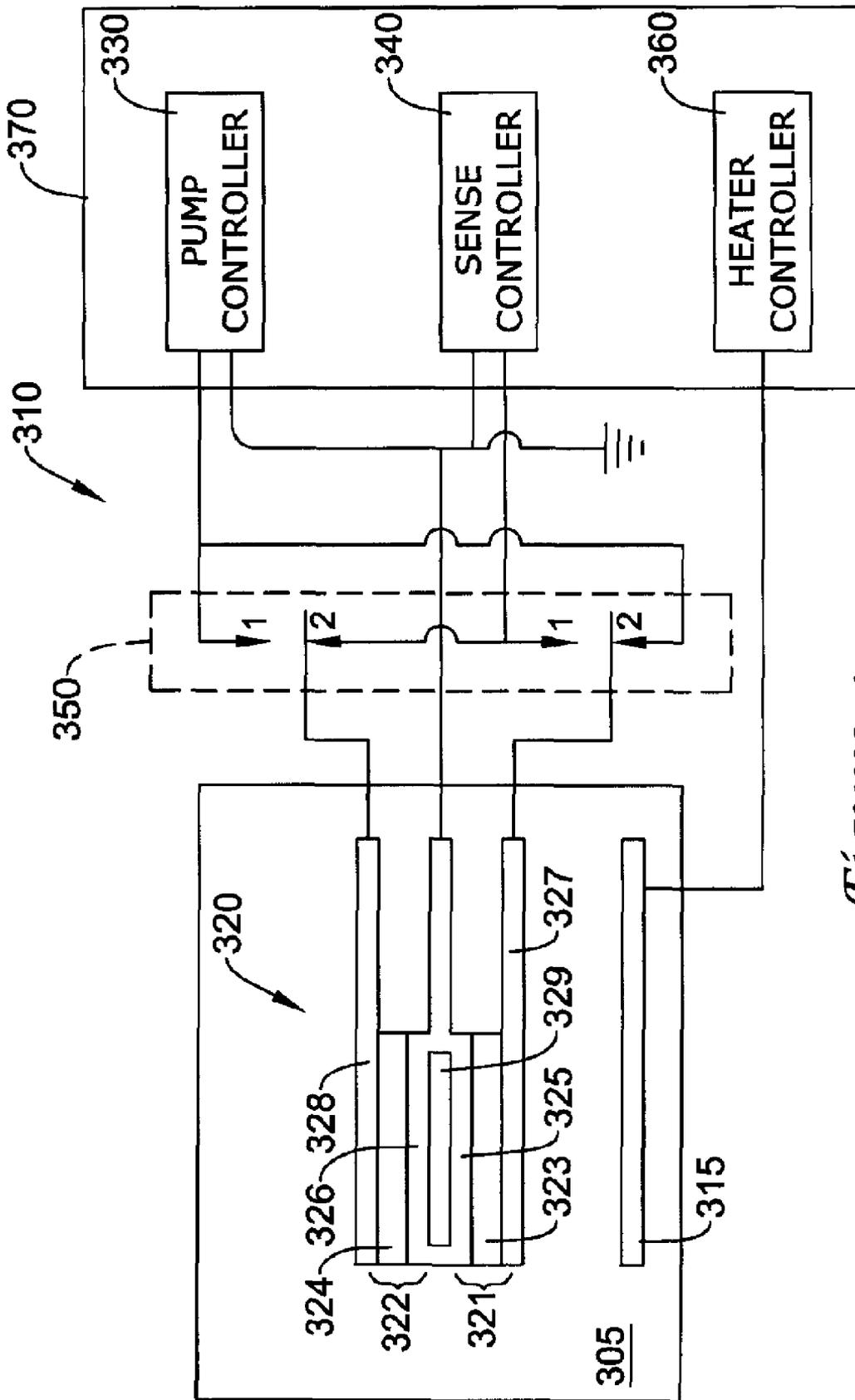


Figure 4

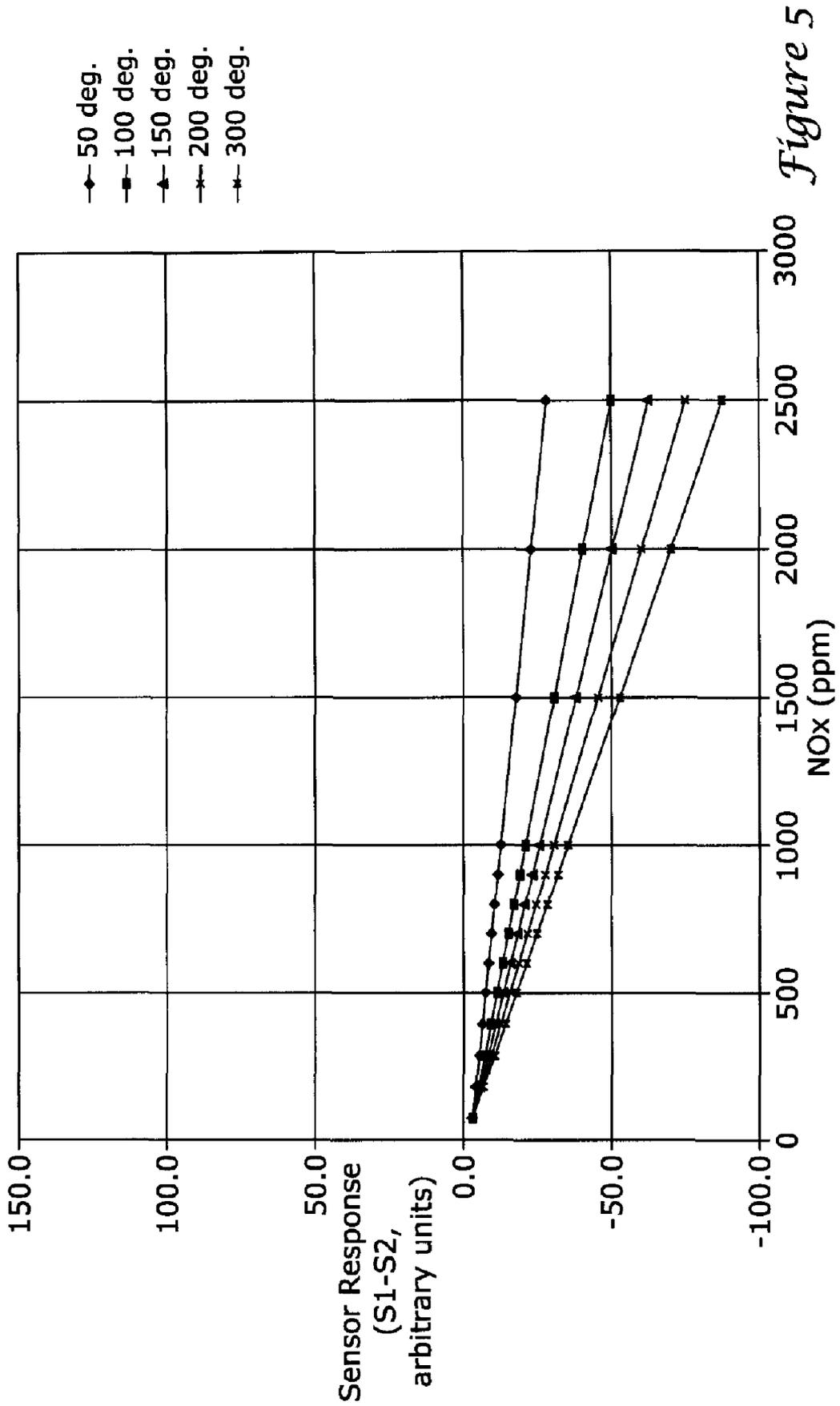


Figure 5

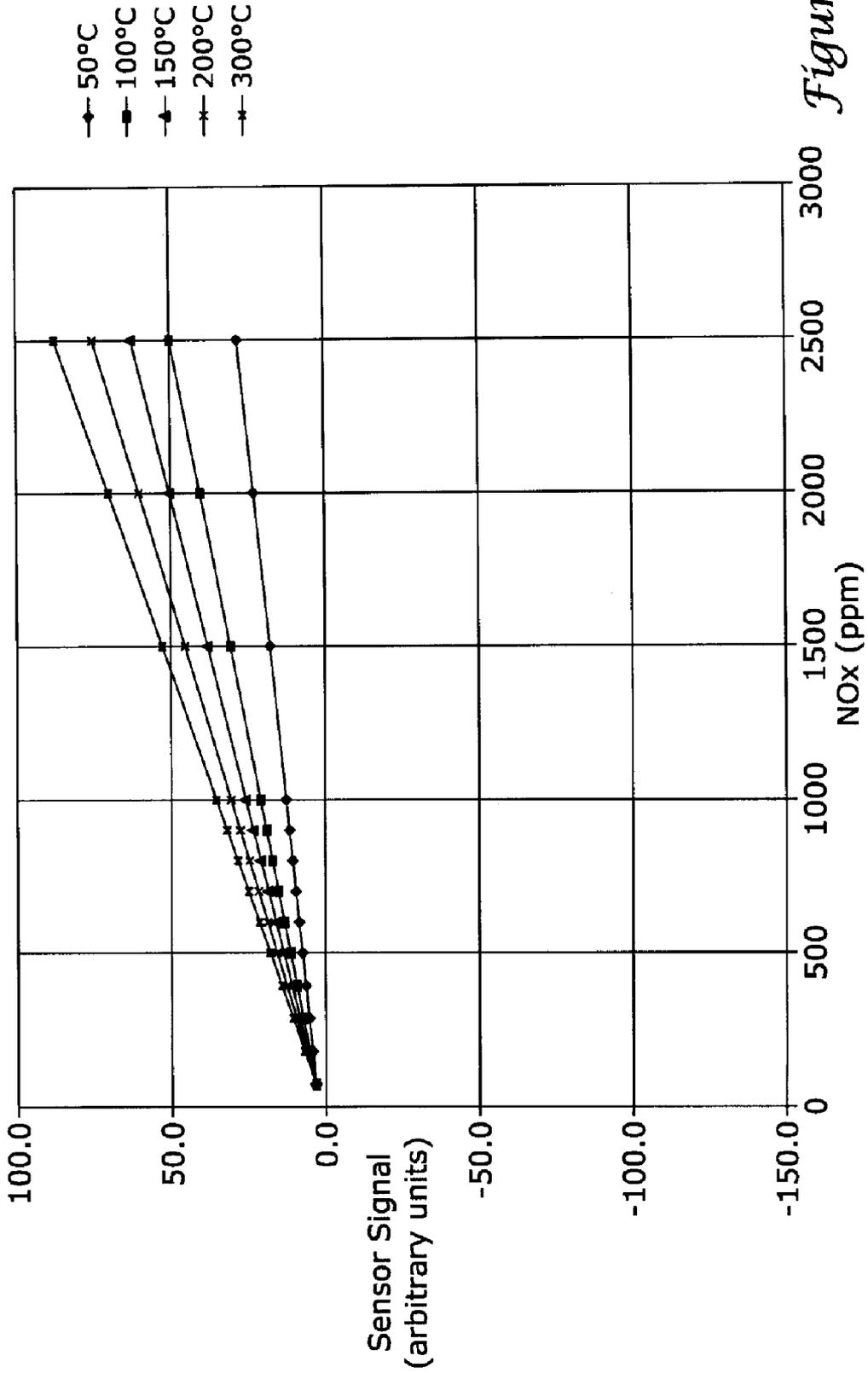


Figure 6

OXIDES OF NITROGEN GAS SENSORS AND METHODS

BACKGROUND

The present invention generally relates to gas sensors and methods of determining the concentration of gaseous components, and in some cases, to sensors and methods for determining the concentration of oxides of nitrogen (NO_x) in a gaseous atmosphere.

Sensors for determining the oxygen composition of gaseous mixtures, such as engine exhaust, are known to the art. For example, U.S. Pat. Nos. 4,272,329, 4,272,330, and 4,272,331 teach an oxygen sensor including a pump cell and a sensor cell, each having solid zirconia electrolyte and thin platinum electrodes attached thereto. The sensor cell and the pump cell, along with a ceramic tube, form an enclosed volume in which the ambient air establishes equilibrium by means of a leak opening in the ceramic tube. The pump cell is connected, by external circuitry, to an electrical input, while the sensor cell is coupled, by external circuitry, to electrical output measurement and control means.

The oxygen sensor taught by the '329 patent is operated in a steady-state mode whereby voltage is applied to the pump cell to electrochemically pump oxygen from the enclosed volume until a steady-state is reached wherein the rate of oxygen pumped from the volume is in equilibrium with the rate of oxygen diffusing into the volume through the leak hole. At steady-state, the oxygen partial pressure in the enclosed volume is reduced from ambient, causing an EMF to develop across the electrodes of the sensor cell. By adjusting the pump cell current to provide a constant sensor cell voltage, the pump cell current is linearly proportional to the percentage oxygen in the ambient atmosphere.

The oxygen sensor taught by the '330 patent uses a similar device operated in a transient mode to measure oxygen partial pressure. After ambient atmosphere of a desired oxygen partial pressure is established in the enclosed volume, the pump cell is activated to withdraw oxygen from the enclosed space. Reduction of oxygen partial pressure in the enclosed space causes an EMF to develop across the sensor cell. The first derivative of sensor cell voltage/time evaluated at or shortly after the initiation of a voltage drop is inversely proportional to the ambient oxygen partial pressure. The oxygen sensor may also be operated by pumping oxygen into the enclosed space and reversing the sign of the initial sensor cell voltage to determine the ambient oxygen partial pressure.

The oxygen sensor taught by the '331 patent uses a similar device operated in an oscillatory mode whereby a repetitive sequence of oxygen pumping currents flow to the pump cell in response to voltage inputs from the sensor cell. The pump cell withdraws oxygen from the enclosed space until the voltage drop induced at the sensor cell equals a predetermined reference value. The polarity of the pump cell current is then reversed to pump oxygen into the enclosed space until the sensor cell voltage reaches another predetermined reference value, at which time the pump cell current is again reversed and the cycle is repeated. With the magnitude of the pump cell current fixed, the period of oscillation is proportional to the oxygen partial pressure.

Sensors for determining the oxides of nitrogen (NO_x) composition of gaseous mixtures, such as engine exhaust, are known to the art. For example, U.S. Pat. No. 6,344,134, discloses a method of measuring NO_x concentration using a two-serial-space NO_x sensor. The sensor includes a first pumping cell and a second pumping cell each comprising a solid electrolyte. In the sensor, a measurement gas space, a

first space, and a second space communicate in series with each other. The method includes the steps of: pumping out oxygen from the first space into, for example, the measurement gas space, or pumping oxygen into the first space from, for example, the measurement gas space by action of the first pumping cell so that the oxygen concentration in the vicinity of a gas inlet of the second space becomes such that a portion of NO in the first space dissociates; dissociating residual NO and O_2 in gas introduced into the second space from the first space by action of the second pumping cell; pumping out oxygen ions generated by dissociation of NO and O_2 from the second space by action of the second pumping cell; and determining the concentration of NO_x in the measurement gas based on signals (for example, pumping currents) issued from the first and second pumping cells.

Existing oxide-based gas sensors do not meet either performance or cost needs to address new environmental regulations, particularly with regard to engine exhaust. Improved oxide-based gas sensors are desired.

SUMMARY

The present disclosure generally relates to gas sensors and methods of determining the concentration of gaseous components, and in some cases, to sensors and methods for determining the concentration of oxides of nitrogen (NO_x) in a gaseous atmosphere.

In one illustrative embodiment, a method for measuring gas component concentrations is disclosed. The method includes the steps of providing a gas stream having a NO concentration and a NO_2 concentration, wherein a sum of the NO concentration and the NO_2 concentration is a total NO_x concentration; contacting the gas stream with a first zirconium oxide based oxygen sensor at a first temperature to achieve a first $\text{NO}:\text{NO}_2$ equilibrium at the first temperature; contacting the gas stream with a second zirconium oxide based oxygen sensor at a second temperature to achieve a second $\text{NO}:\text{NO}_2$ equilibrium at the second temperature; and determining the total NO_x concentration by measuring a response of the first zirconium oxide based oxygen sensor to achieve the first $\text{NO}:\text{NO}_2$ equilibrium and a response of the second zirconium oxide based oxygen sensor to achieve the second $\text{NO}:\text{NO}_2$ equilibrium. The second temperature is different than the first temperature.

In another embodiment, a method includes the steps of providing a gas stream having a NO concentration and a NO_2 concentration at a first $\text{NO}:\text{NO}_2$ equilibrium at a first temperature, wherein the total of the NO concentration and the NO_2 concentration is a total NO_x concentration; contacting the gas stream with a zirconium oxide based oxygen sensor at a second temperature to achieve a second $\text{NO}:\text{NO}_2$ equilibrium at the second temperature, the second temperature is different than the first temperature; and determining the total NO_x concentration by measuring a response of the zirconium oxide based oxygen sensor to achieve the second $\text{NO}:\text{NO}_2$ equilibrium.

In still a further embodiment, NO_x sensor apparatus includes a first zirconium oxide based oxygen sensor in fluid connection with a NO_x gas source and in electrical connection with a sensor controller. The first zirconium oxide based oxygen sensor includes a first platinum sense electrode. A heating element is in thermal communication with the first zirconium oxide based oxygen sensor. A second zirconium oxide based oxygen sensor is in fluid connection with the NO_x gas source and in electrical connection with the sensor controller. The first zirconium oxide based oxygen sensor includes a second platinum sense electrode.

In a further embodiment, an NO_x sensor apparatus includes a porous media including a catalyst that assists in NO+½O₂↔NO₂ equilibrium and in fluid communication with a NO_x gas source. A zirconium oxide based oxygen sensor in fluid communication with the porous media and in electrical connection with a sensor controller. The zirconium oxide based oxygen sensor includes a platinum sense electrode and a heating element is in thermal communication with the first zirconium oxide based oxygen sensor.

These and other aspects of the present application will be apparent from the detailed description below. In no event, however, should the above summaries be construed as limitations on the claimed subject matter, which subject matter is defined solely by the attached claims, as may be amended during prosecution.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention may be more completely understood in consideration of the following detailed description of various embodiments of the invention in connection with the accompanying drawings, in which:

FIG. 1 is a diagrammatic plan view of an illustrative NO_x sensor apparatus;

FIG. 2 is a diagrammatic plan view of another illustrative NO_x sensor apparatus;

FIG. 3 is a schematic cross-sectional view of an illustrative zirconium oxide based oxygen sensor device in a first position;

FIG. 4 is a schematic cross-sectional view of an illustrative zirconium oxide based oxygen sensor device in a second position;

FIG. 5 is an illustrative graph of sensor response verses concentration of NO_x for the sensor apparatus shown in FIG. 1; and

FIG. 6 is an illustrative graph of sensor response verses concentration of NO_x for the sensor apparatus shown in FIG. 2.

While the invention is amenable to various modifications and alternative forms, specifics thereof have been shown by way of example in the drawings and will be described in detail. It should be understood, however, that the intention is not to limit the invention to the particular illustrative embodiments described. On the contrary, the intention is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the invention.

DETAILED DESCRIPTION

The following description should be read with reference to the drawings, in which like elements in different drawings are numbered in like fashion. The drawings, which are not necessarily to scale, depict selected embodiments and are not intended to limit the scope of the invention. Although examples of construction, dimensions, and materials may be illustrated for the various elements, those skilled in the art will recognize that many of the examples provided have suitable alternatives that may be utilized.

Generally, the present invention pertains to gas sensors and methods of determining the concentration of oxides on nitrogen (NO_x) in a gaseous atmosphere. While the present invention is not so limited, an appreciation of various aspects of the invention will be gained through a discussion of the various illustrative embodiments and examples provided below.

Oxides of nitrogen concentrations in a gas are generally governed by the equilibrium:



In addition, at equilibrium the ratio of NO₂ to NO can be predicted from the equation:

$$(\text{pNO}_2)/\text{pNO} = 1.6 \times 10^{-4} \cdot \exp(13,900/\text{RT}) \cdot (\text{pO}_2)^{1/2}$$

For example, at 750 degrees centigrade and 1% excess oxygen, the equilibrium ratio is 0.01503 (i.e., 98.5% NO and 1.5% NO₂). Thus, at any specified temperature and known oxygen concentration, at equilibrium the ratio of NO₂ to NO can be predicted.

The oxygen sensors described herein provide a response to gas samples that have an initial non-equilibrium ratio of NO₂ to NO at the sensor temperature to monitor the approach toward the equilibrium ratio of NO₂ to NO at the sensor temperature. In some embodiments, the sensor apparatus uses two zirconium oxide based oxygen sensors or alternatively one zirconium oxide based oxygen sensor and a catalytic porous membrane, all maintained at known temperatures, to monitor the approach toward the equilibrium ratio of NO₂ to NO at the individual sensor temperature. By maintaining the elements at different temperatures, different equilibria are approached without need to know the gas source initial conditions. Competing reactions such as from, for example, carbon monoxide and methane, proceed to completion and do not interfere with the determination of total NO_x.

FIG. 1 is a diagrammatic plan view of an illustrative NO_x sensor apparatus **100**. The sensor **100** includes a first zirconium oxide based oxygen sensor **110** (described below) in fluid connection with a NO_x gas source **F** and in electrical connection with a sensor controller **140**. A second zirconium oxide based oxygen sensor **120** is in fluid connection with the NO_x gas source **F** and is also in electrical connection with the sensor controller **140**. In many embodiments, the sensor apparatus **100** includes a housing **130** disposed about the first zirconium oxide based oxygen sensor **110** and the second zirconium oxide based oxygen sensor **120**. In some embodiments, a porous media including a catalyst that assists in NO+½O₂↔NO₂ equilibrium is in fluid communication with a NO_x gas source **F** and disposed between the gas source **F** and the first zirconium oxide based oxygen sensor **130** or the second zirconium oxide based oxygen sensor **140**.

In operation, the illustrative NO_x sensor apparatus **100** functions by providing a gas stream **101** having a NO concentration and a NO₂ concentration and contacting the gas stream **101** with the first zirconium oxide based oxygen sensor **110** at a first temperature to achieve a first NO:NO₂ equilibrium at the first temperature, and contacting the gas stream **101** with a second zirconium oxide based oxygen sensor **120** at a second temperature to achieve a second NO:NO₂ equilibrium at the second temperature. The second temperature is different than the first temperature. The sum of the NO concentration and the NO₂ concentration is a total NO_x concentration. Total NO_x concentration is determined by measuring the response of the first zirconium oxide based oxygen sensor **110** to achieve the first NO:NO₂ equilibrium and the response of the second zirconium oxide based oxygen sensor **120** to achieve the second NO:NO₂ equilibrium. In many embodiments, the gas stream **101** includes oxygen at an oxygen concentration. An exiting gas stream **103** is shown flowing away from the first and second zirconium oxide based oxygen sensors **110**, **120**.

In many embodiments, the first zirconium oxide based sensor **110** and/or the second zirconium oxide based sensor **110** includes a catalyst that assists in providing the gas stream having a specified NO:NO₂ equilibrium (NO+½O₂↔NO₂) at each specified temperature. The catalyst can be any useful catalyst as described below.

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In some embodiments, total NO_x concentration is determined by measuring a difference of the response of the first zirconium oxide based oxygen sensor **110** to achieve the first $\text{NO}:\text{NO}_2$ equilibrium and the response of the second zirconium oxide based oxygen sensor **120** to achieve the second $\text{NO}:\text{NO}_2$ equilibrium. FIG. **5** is an illustrative graph of sensor response verses concentration of NO_x for the sensor apparatus **100** shown in FIG. **1**.

FIG. **2** is a diagrammatic plan view of another illustrative NO_x sensor apparatus **200**. The sensor apparatus **200** includes a porous media **210** that includes a catalyst that assists in $\text{NO}+\frac{1}{2}\text{O}_2\leftrightarrow\text{NO}_2$ equilibrium and in fluid communication with a NO_x gas source F. The catalyst can be any useful catalyst as described below. A zirconium oxide based oxygen sensor **220** (described below) is in fluid communication with the porous media **210** and in electrical connection with a sensor controller **240**. An optional heating element **215** is shown thermal communication with the porous media **210**.

In operation, the illustrative NO_x sensor apparatus **200** functions by providing a gas stream **202** having a NO concentration and a NO_2 concentration at a first $\text{NO}:\text{NO}_2$ equilibrium at a first temperature and contacting the gas stream **202** with a zirconium oxide based oxygen sensor **220** at a second temperature to achieve a second $\text{NO}:\text{NO}_2$ equilibrium at the second temperature. The second temperature is different than the first temperature. The sum of the NO concentration and the NO_2 concentration is a total NO_x concentration. The total NO_x concentration can be determined by measuring a response of the zirconium oxide based oxygen sensor **220** to achieve the second $\text{NO}:\text{NO}_2$ equilibrium. An exiting gas stream **203** is shown flowing away from the zirconium oxide based oxygen sensor **220**.

In many embodiments, the gas stream **202** is provided by flowing source gas **201** through a porous media **210** including a catalyst, at a first temperature, that assists in providing the first $\text{NO}:\text{NO}_2$ equilibrium at the first temperature. The catalyst can be any useful catalyst as described below. In many embodiments, the gas stream **202** includes oxygen at an oxygen concentration. FIG. **6** is an illustrative graph of sensor response verses concentration of NO_x for the sensor apparatus **200** shown in FIG. **2**.

FIG. **3** is a schematic cross-sectional view of an illustrative zirconium oxide based oxygen sensor **310** in a first position **1**. The gas sensor **310** includes a sensor element **320** electrically coupled to a pump controller **330** and a sense controller **340**. As used herein, the term "controller" refers to electronics and/or software. The sensor element **320** is disposed within a first space **305** in fluid communication with a gas source containing one or more gases to be measured by the sensor element **320**, such as, for example oxygen and oxides of nitrogen. In many embodiments, the gases to be measured are NO and NO_2 or NO_x respectively, where $\text{NO}_x=\text{NO}+\text{NO}_2$. An optional heating element **315** is shown electrically coupled to a heater controller **360** and in thermal communication with the sensor **310**. The heating element **315** can modify a temperature at which the sensor element **320** senses at. In the illustrative embodiment shown, the pump controller **330**, sense controller **340**, and the heater controller **360** are disposed within a controller module **370**, but this is not required. The sensor element **320** includes a first cell **321** and a second cell **322**. The sensor element **320** can be any configuration such as, for example, cylindrical or planar.

The first cell **321** includes an oxygen-ion conductive solid electrolyte layer **323** such as a zirconium oxide layer disposed between two first cell conductive electrodes **325** and **327**. In one embodiment, the first cell conductive electrodes **325** and **327** are first cell platinum electrodes **325**, **327**. In some

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embodiments, the first cell electrode **327** includes a catalyst **319** that assists in $\text{NO}+\frac{1}{2}\text{O}_2\leftrightarrow\text{NO}_2$ equilibrium. The catalyst **319** can be any useful catalyst such as, for example, gold, nickel, or rhodium. The catalyst **319** can be a layer of catalyst disposed on an outer surface of the first cell electrode **327**. In many embodiments, the catalyst **319** is formed in a layer from 0.1 to 5 micrometers thick and can be applied by any useful deposition technique.

The second cell **322** includes an oxygen-ion conductive solid electrolyte layer **324** such as a zirconium oxide layer disposed between two second cell conductive electrodes **326** and **328**. In some embodiments, both of the second cell conductive electrodes **326** and **328** are second cell platinum electrodes **326** and **328**. In one embodiment, the first cell **321** and second cell **322** inner electrodes **325** and **326** is a common platinum electrode. A sealed measurement space **329** is disposed within the sensor element **320**.

FIG. **3** shows the sensor element **320** electrically coupled to the pump controller **330** and sense controller **340** in a first position **1**. In this embodiment, the first cell **321** is electrically coupled to the pump controller **330** and the second cell **322** is electrically coupled to the sense controller **340**. In one embodiment, the first cell **321** has a layer of zirconium oxide **323** disposed between the outer electrode **327** and the inner electrode **325**; the second cell **322** has a layer of zirconium oxide **324** disposed between the outer electrode **328** and the inner electrode **326**. In this configuration, a total NO_x gas concentration can be determined.

In some embodiments, the pump controller **330** and the sense controller **340** can be optionally switched to be electrically coupled to either the first cell **321** or second cell **322** via a switching element **350**, as shown in FIG. **4** wherein the sensor element **320** is electrically coupled to pump controller **330** and sense controller **340** in a second position **2**. In this configuration, oxygen concentration can be measured.

The switching element **350** can be controlled by hardware and/or software capable of switching the electrical signal routing from the first cell **321** and second cell **322** to the pump controller **330** and the sense controller **340**. Pump controllers **330** and sense controllers **340** are well known in the art. When a pump controller **330** is electrically coupled to, for example, the first cell **321**, and a pumping current is applied, ion pumping action takes place between the first cell electrodes **325** and **327**. Concurrently, the second cell electrodes **326** and **328** cooperate to detect an electromotive force induced therebetween, as is known.

The present invention should not be considered limited to the particular examples described above, but rather should be understood to cover all aspects of the invention as fairly set out in the attached claims. Various modifications, equivalent processes, as well as numerous structures to which the present invention can be applicable will be readily apparent to those of skill in the art to which the present invention is directed upon review of the instant specification.

What is claimed is:

1. A method of calculating a total NO_x concentration, comprising steps of:
 - providing a gas stream having a NO concentration and a NO_2 concentration, wherein a sum of the NO concentration and the NO_2 concentration is a total NO_x concentration;
 - contacting the gas stream with a first zirconium oxide based oxygen sensor at a first temperature to measure a first oxygen concentration and then using the first oxygen concentration to predict a first ratio of $\text{NO}:\text{NO}_2$ at equilibrium at the first temperature;

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contacting the gas stream with a second zirconium oxide based oxygen sensor at a second temperature to measure a second oxygen concentration and then using the second oxygen concentration to predict a second ratio of NO:NO₂ at equilibrium at the second temperature, the second temperature being different than the first temperature; and

calculating the total NO_x concentration using the first ratio of NO:NO₂ at equilibrium and the second ratio of NO:NO₂ at equilibrium.

2. A method of calculating the total NO_x concentration according to claim 1 wherein the providing a gas stream step comprises providing a gas stream further comprising an oxygen concentration.

3. A method of calculating the total NO_x concentration according to claim 1 wherein the contacting the gas stream with a first zirconium oxide based sensor step comprises contacting the gas stream with a first zirconium oxide based sensor comprising a catalyst that assists in providing the gas stream having the first ratio of NO:NO₂ at equilibrium at the first temperature.

4. A method of calculating the total NO_x concentration according to claim 1 wherein the contacting the gas stream with a second zirconium oxide based sensor step comprises contacting the gas stream with a second zirconium oxide based sensor comprising a catalyst that assists in providing the gas stream having the second ratio of NO:NO₂ at equilibrium at the second temperature.

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5. A method of calculating the total NO_x concentration according to claim 1 wherein the contacting the gas stream with a first zirconium oxide based sensor step comprises contacting the gas stream with a first zirconium oxide based sensor comprising a catalyst that assists in providing the gas stream having the first ratio of NO:NO₂ at equilibrium at the first temperature and the contacting the gas stream with a second zirconium oxide based sensor step comprises contacting the gas stream with a second zirconium oxide based sensor comprising a catalyst that assists in providing the gas stream having the second ratio of NO:NO₂ at equilibrium at the second temperature.

6. A method of calculating the total NO_x concentration according to claim 1 wherein the calculating step comprises measuring a difference of the response of the first zirconium oxide based oxygen sensor to achieve the first ratio of NO:NO₂ at equilibrium and the response of the second zirconium oxide based oxygen sensor to achieve the second ratio of NO:NO₂ at equilibrium.

7. A method according to claim 1 wherein the contacting step comprises contacting the gas stream with a zirconium oxide based oxygen sensor comprising a catalyst that assists in providing the gas stream having a NO concentration and a NO₂ concentration at the second ratio of NO:NO₂ at equilibrium at the second temperature.

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